Chrome Liquor Recycling in Pigskin Tanning

Tomoyoshi KUBO and Yasuhiro ISHII

Tokyo Noko University, Faculty of Agriculture, Scleroprotein
and Leather Research Institute, Fuchu-shi 183

(Received October 23, 1980)

Abstract Using technical experience in chrome liquor recycling for cattle-hide leather manufacture, applicability of the recycling system to pigskin tanning was investigated. When pigskins were tanned with sulfite-reduced chrome agent, the general composition and chrome complexes in spent chrome liquor recycled indicated no significant variations during sequential 11 runs of tanning. Moreover, the recycling of spent chrome liquor did not affect the chemical composition, mechanical strengths, and stiffness of resultant leather processed as the soft type pigskin leather. It was concluded that the chrome liquor recycling in pigskin tanning as well as in cattle-hide tanning could be recommended to put in practice.

Jpn. J. Zootech. Sci., 52 (4): 308-313, 1981

Although pigskin are abundantly produced in Japan, only a limited number of research on the techniques for developing its leather-making potentiality has been reported. The authors have suggested some technical improvements for beamhouse operation in the previous papers¹⁻³⁾ in a series of studies on pigskin leather-manufacturing techniques.

In the field of cattle-hide leather manufacture, the recycling of spent chrome liquor is recommended for reducing tannery effluent pollution and saving the chrome resources⁴⁾. DAVIS and SCROGGIE⁵⁻⁸⁾, BURNS *et al.*⁹⁾, FRANCE¹⁰⁾, PIERCE and THORSTENSEN¹¹⁾, BARLOW and IP¹²⁾, and NIWA *et al.*¹³⁾ already reported that the recycling did not affect the salt composition of spent chrome liquor and mechanical strength and quality of resultant leather substantially. The authors¹⁴⁾ also have reported that there is essentially no difficulty in the chrome liquor recycling from the study on its chrome complex composition.

When chrome tanning of pigskin is carried out, it may be less protected against relatively minor changes in the chrome liquor composition during recycling, because the structure of pigskin collagen is less stabilized compared with cattle-hide collagen¹⁵⁾. Therefore, the effectiveness of chrome liquor recycling in pigskin tanning should be ascertained by more sensitive examinations of the mechanical property of leather. In the viewpoint described, the properties of pigskin leather produced from recycled chrome liquor were investigated in the present experiment.

Materials and Methods

Chrome tanning and the recycling of spent chrome liquor

After wet salted pigskins (4.1 kg/piece) were soaked, limed, bated, and pickled

Chrome Liquor Recycling in Pigskin Tanning

Table 1. Procedures of chrome tanning

Material	: wet salted pigskin (4.1 kg/piece)
Wash	: with 300% water for 20 minutes and with running water for 30 minutes
Soak	: with 300% water and 0.8% sodium bicarbonate overnight
Lime	: with 300% water, 3% sodium hydrosulfide, 0.8% sodium sulfide, 5% calcium hydroxide, and 0.3% nonionic surfactant overnight and split
Relime	: with 400% water, 4% calcium hydroxide, 0.2% nonionic surfactant for 48 hours with intermediate scudding and weigh (% on salted weight basis)
Delime/bate	: with 300% water (33°C) and 2% ammonium chloride for 30 minutes, add 0.08% bating agent and 0.92% ammonium chloride, then run for 2 hours, pH 8.65
Pickle	: with 80% water, 8% sodium chloride, 1.5% sulfuric acid diluted with 10% water overnight, pH 2.85
Tanning	: with 30% water, 3% sodium chloride, and 8% chrome agent* for 30 minutes and 0.88% sodium bicarbonate, then run for 60 minutes at 30°C, add 60% water and run for 2 hours at 35°C and for 60 minutes at 40°C, final pH 3

* Neochrome A from Nippon Denko Corp. (sulfite-reduced chrome agent)

under the condition given in Table 1, 10 kg portion of pickled stock (equivalent to 15 kg in the limed weight) was subjected to chrome tanning as shown in Table 1. The spent chrome liquor was recovered and used for the base of tanning float of the subsequent tanning run. Thus, for the second and the subsequent runs, float of 90% water, 3% sodium chloride, and 10% chrome agent was replaced by that of 10% water and 80% spent liquor from the preceding run with supplemental addition of chrome agent to maintain the same chrome concentration. The tanning condition was same as that in the first run of tanning.

Analyses of spent chrome liquor

Spent chrome liquors were subjected to the following analyses after passing through 60-mesh screen and filterpaper of analytical grade.

COD (bichromate method) and pH were determined according to SMEWW method¹⁶⁾, chrome content and basicity according to ALCA method. Contents of sodium ion and chloride ion were determined by using specific ion-sensitive electrodes from Orion Corp., sodium ion electrode 94-11 and chloride ion electrode 94-17, respectively. Content of sulfate ion was determined by benzidine method and content of coordinate sulfate was calculated from the difference between contents of ionic and total sulfate determined gravimetrically after boiling the chrome liquor in 10% acetic acid solution for 60 minutes.

Charge distribution of chrome complexes in the liquor was characterized by fractionation on cation exchanging column, Dowex-50W-X1, 100-mesh, Na-form; fraction 1 had no affinity to the resin, fraction 2 eluted with 0.1 N HCl from the column and tentatively classified as $[\text{Cr}]^+$ complex, fraction 3 eluted with 3 N HCl and classified as $[\text{Cr}]^{+++}$ complex, and fraction 4 eluted with 6 N HCl and was classified as highly solated complex¹⁷⁾. Relative proportion of these fractions was calculated on the basis of chrome content.

Table 2. Neutralization, retanning, and fatliquoring of shaved stock (1 mm thickness)

Wash	: with running water at 40°C for 10 minutes
Neutralize/retan:	with 200% water at 40°C, 0.2% acetic acid, 1.5% glutaraldehyde agent* ¹ diluted with 3% water, 4% chrome agent* ² for 90 minutes at pH 3.5, add 1% Neutrigan diluted with 10% water, run for 30 minutes at pH 4
Wash	: with running water at 40°C for 5 minutes
Pre-treat	: with 200% water at 40°C and 2% leveling agent* ³ for 30 minutes at pH 4.6
Wash	: with running water for 5 minutes
Fatliquor	: with 200% water at 40°C, 5% fatliquoring agent* ⁴ diluted with 30% water at 40°C for 30 minutes

*¹Relugan GT-50 from BASF Corp. *²Chromitan MS from BASF Corp, of high basicity

*³Neutrigan from BASF Corp. *⁴Mixture of 2 parts Eukesol fatliquor 1 (sulfited fish oil), 2 parts Eukesol fatliquor SAF (anionic, synthetic oil), and 1 part Eukesol fatliquor A (anionic surfactant)

Processing of chrome leather

Chrome tanned stocks of different tanning runs were collected together into a lot after storage for a month packed in plastics bags in order to diminish the influence of the variation of time lapse after tanning, and neutralized, retanned, and fatliquored for soft-type chrome leather under the condition as shown in Table 2. They were then hang-dried and toggled.

Physical testing and chemical analysis of leather

Examinations were carried out by using specimen 20×20 cm collected from butt portion of dried leather. Tensile and tongue tear strengths and elongation at break were measured according to ALCA method.

Results and Discussion

The general composition of spent chrome liquors recycled is shown in Table 3 and

Table 3. General composition of spent chrome liquor in recycling

Run No. of tanning	Weight of added chrome agent g	Composition of spent liquor						
		chrome Cr ₂ O ₃ g/l	basicity %	pH	COD %*	Na ⁺ %*	Cl ⁻ %*	SO ₄ ⁼ %*
1	1200	14.3	43	3.0	100 (688 ppm)	100 (0.91 mol/l)	100 (0.68 mol/l)	100 (0.27 mol/l)
2	512	10.7	46	3.1	117	80	91	98
3	687	8.4	44	3.1	123	79	85	99
4	797	10.7	47	3.2	149	87	87	114
5	688	9.8	47	3.1	175	85	85	112
8	701	10.7	43	3.1	172	86	85	115
11	672	10.8	46	3.0	151	90	90	112

15 kg pelts and 13.5 l tanning liquor were used for each run. * based on the content of run No. 1 spent liquor

Chrome Liquor Recycling in Pigskin Tanning

Table 4. Compositions of chrome complex in recycled spent liquors

Run No. of tanning	Basicity (%)	Fractionation of chrome complexes on cation exchanging column (% mole fraction)				Sulfato group of chrome complexes (% equivalent to chrome)
		fraction 1	fraction 2	fraction 3	fraction 4	
Original liquor	33	60	9	28	3	
Original liquor	48	21	5	62	12	
Spent liquor						
run No. 1	43	16	8	68	9	21
2	46	14	8	70	9	13
3	44	16	8	64	11	11
4	47	19	9	64	9	18
5	47	17	6	64	13	16
8	43	17	8	69	7	21
11	46	17	8	66	9	24

the fractional proportion of chrome complexes on cation exchanging column is shown in Table 4.

Except for the increase of COD in early runs of tanning, the content of general components such as chrome, sodium, chloride, and sulfate ions demonstrates no significant variation by recycling spent chrome liquor.

Compositions of chrome complex in recycled spent liquors also indicate only small variations during sequential 11 runs of tanning and are in such a good similarity to that of the original chrome liquor of basicity 48% as observed between the original and recycled chrome liquors in cattle-hide tanning experiment⁽⁴⁾. This means that the over-all sorption of chrome complexes by pelt is less selective. This is due to the rapid establishment of the equilibrium in spite of selective sorption of individual

Table 5. Chemical composition of pigskin leathers produced from recycled chrome liquors

Run No.	Moisture %	Hide substance* %	Fat* %	Ash* %	Chrome* Cr ₂ O ₃ %	pH
1	15.8	80.1	3.3	5.9	5.0	3.3
2	14.0	80.8	3.5	5.8	5.0	3.3
3	15.7	75.5	6.0	5.9	5.0	3.2
4	15.9	78.4	4.5	6.0	5.3	3.3
5	16.6	79.2	4.0	5.8	4.8	3.3
6	16.0	79.6	3.8	5.9	5.2	3.3
7	15.0	80.1	4.2	5.8	4.9	3.3
8	14.5	79.2	4.3	5.9	5.0	3.4
9	14.8	78.1	4.4	5.8	5.0	3.3
10	17.0	82.8	3.6	5.6	4.9	3.3
11	16.0	80.4	3.5	5.7	4.8	3.3

* on the dry weight basis

chrome compounds. Such nature of chrome sorption is probably one of factors in favor of stabilizing the composition of chrome complexes in spent liquor during recycling.

Chemical compositions of pigskin chrome leathers obtained from recycled chrome liquors are shown in Table 5.

Except for fat content, chemical composition of leather indicates only small variations with recycling and no significant influence of the recycling. Although fat content for run No. 3 is abnormally high, this is probably considered as a contribution not by recycling chrome liquor but by the abnormally small thickness of shaved leather (0.75 mm for run No. 3 against 0.8–0.9 mm for other runs). The possible explanation is that the thinner shaved leather receives the stronger strain by the same mechanical motion in the drum and so records an enhanced sorption of fat from fatliquoring bath¹⁸⁾. Therefore, no influence by recycling chrome liquor is observed from the general view of chemical composition of resultant leather.

Tensile and tear strengths, elongation at break, and stiffness by Gurley method are shown in Table 6.

Table 6. Mechanical properties of pigskin leathers produced from recycled chrome liquors

Run No.	Strength				Elongation		Stiffness by Gurley (10 mg)			
	tensile	(kg/mm ²)	tongue tear	(kg/mm)	at break (%)		grain	side-in	grain	side-out
	$\bar{X}$	SD	$\bar{X}$	SD	$\bar{X}$	SD	$\bar{X}$	SD	$\bar{X}$	SD
1	1.5	0.2	1.5	0.4	49	7	274	73	203	19
2	1.5	0.4	1.5	0.4	47	7	246	56	203	13
4	1.5	0.3	1.6	0.5	50	8	258	67	207	26
5	1.4	0.4	1.4	0.3	41**	8	250	59	200	24
6	1.5	0.2	1.3	0.3	48	9	284	63	216	38
7	1.4	0.3	1.4	0.3	46	5	270	68	203	14
8	1.4	0.3	1.4	0.3	47	9	264	76	208	24
9	1.4	0.3	1.4	0.4	47	8	272	72	210	18
10	1.4	0.3	1.7	0.5	48	8	262	67	219	39
11	1.6	0.2	1.8	0.6	52	9	320**	76	245**	59

** The difference against the run No. 1 value is significant by 1% level.

Data for run No. 3 have been omitted from the table because this lot of leather has the defects of abnormal thickness and fat content described above. The difference of average value of tensile and tear strengths and elongation between run No. 1 and a run of No. 4 to No. 11 was statistically insignificant. For stiffness, which may be considered as a more sensitive parameter concerning physical condition of leather¹⁹⁾, the difference from run No. 1 was also insignificant except for run No. 11. Although the reason of slightly higher stiffness of run No. 11 leather can not be exactly explained, variations of operational conditions among these lots may be involved.

As a conclusion, the recycling of chrome liquor in pigskin tanning does not affect the properties of pigskin leather and can also be recommended to put in practice.

References

- 1) KUBO, T. and K. SHIRAI, Jpn. J. Zootech. Sci., **51**: 100-104. 1980.
- 2) KUBO, T. and K. SHIRAI, Jpn. J. Zootech. Sci., **51**: 279-283. 1980.
- 3) KUBO, T., K. SHIRAI and K. WADA, HIKAKU-KAGAKU, **25**: 237-240. 1980.
- 4) HAUCK, R. A., J. Am. Leather Chem. Ass., **67**: 422-429. 1972.
- 5) DAVIS, M. H. and J. G. SCROGGIE, J. Soc. Leather Tech. Chem., **57**: 53-58. 1973.
- 6) DAVIS, M. H. and J. G. SCROGGIE, J. Soc. Leather Tech. Chem., **57**: 81-83. 1973.
- 7) DAVIS, M. H. and J. G. SCROGGIE, J. Soc. Leather Tech. Chem., **57**: 173-176. 1973.
- 8) DAVIS, M. H. and J. G. SCROGGIE, Das Leder, **31**: 1-8. 1980.
- 9) BURNS, J. E., D. E. COLQUITT, M. H. DAVIS and J. G. SCROGGIE, J. Soc. Leather Tech. Chem., **60**: 106-112. 1976.
- 10) FRANCE, H. G., J. Am. Leather Chem. Ass., **70**: 206-216. 1975.
- 11) PIERCE, R. and T. C. THORSTENSEN, J. Am. Leather Chem. Ass., **71**: 161-168. 1976.
- 12) BARLOW, J. R. and H. S. W. IP, J. Soc. Leather Tech. Chem., **61**: 29-33. 1977.
- 13) NIWA, Y., M. KAWAKAMI and I. YOKOKAWA, HIKAKU-KAGAKU, **21**: 232-243. 1975.
- 14) WADA, K., K. SHIRAI and T. KUBO, J. Am. Leather Chem. Ass., under supervision for J. Am. Leather Chem. Ass.
- 15) WADA, K., K. SHIRAI and A. KAWAMURA, J. Am. Leather Chem. Ass., **75**: 90-99. 1980.
- 16) Standard Method for Examination of Water and Waste-Water. 13th ed. 1971. American Public Health Assoc.
- 17) KAWAMURA, A. and K. WADA, J. Am. Leather Chem. Ass., **52**: 476-488. 1957.
- 18) SHIRAI, K., T. CHANG and H. OKAMURA, HIKAKU-KAGAKU, **18**: 13-27. 1972.
- 19) SHIRAI, K. and H. OKAMURA, HIKAKU-KAGAKU, **18**: 203-215. 1973.

豚皮のなめしにおけるクロム液の循環利用

久保知義・石井泰博

東京農工大学農学部硬蛋白質利用研究施設, 府中市 183

豚皮のなめし工程におけるクロム液の循環再利用を牛革の製造における技術的な経験を適用して研究した。すなわち、豚皮の亜硫酸還元クロムなめしにおいてクロム液を 11 回循環再利用してソフトタイプクロム革を製造し、循環に伴うクロム排水の組成と製出革の性状を調べた。クロム排水中のクロム量、pH、ナトリウムイオン、塩素イオン及び硫酸イオン、並びにクロム錯イオンの電

荷分布などの成分組成は 11 回の循環再利用による変動をほとんど示さなかった。また、クロム排水の循環利用による製出革の化学組成、並びに機械的強度と剛軟度への影響は少なかった。以上の結果から、豚皮を対象としたクロムなめしにおける排水の循環利用は、牛皮と同様に実用化が可能である。

日畜会報, **52** (4): 308-313, 1981